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Electronic absorption spectra of 2, 4-dichlorobromobenzene in vapour phase

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The electronic absorption spectra of 2,4-dichlorobromobenzene has been photographed on Hilger medium quartz spectrograph in vapour phase. The observed bands have been explained in terms of three ground state (123, 203 and 427 cm^{-1}) and six excited state (219, 340, 494, 616, 930 and 1097 cm^{-1}) fundamental vibrational frequencies. The 0, 0 band has been identified at 2850·9Å (35066 cm^{-1}).

1. Introduction

It is known that the electronic transition which occurs in benzene in the region 2700–2200 Å appears at longer wavelengths upon substitution. This shift increases more or less regularly in the series of chlorobenzene, dichlorobenzenes and trichlorobenzenes (Sponer 1942, 1947).

Spectroscopic investigations of 1,2,3-trichlorobenzene has been made in hexane solution by Conrad-Billroth (1932). The general range of the spectra is 2600–2950Å. Later on Sponer (1947) made an extensive investigation of electronic transitions in trichlorobenzenes in vapour phase. These studies have drawn the attention of some of the workers to study the effect by replacing one chlorine atom in trichlorobenzene by Bromine atom. Tripathi & Pandey (1972) have studied the electronic transitions in 2,5- and 3.4-dichlorobromobenzenes. With the above in view, the spectral investigation of 2.4-dichlorobromobenzene, which is obtained by replacing one chlorine atom at position 1 by bromine atom in 1,2,4-trichlorobenzene, has been done in the present paper.

2. Experimental Procedure

The chemical obtained from M/s K. Light Laboratories, England, was used as such. The spectra has been photographed on Hilger Medium quartz spectrograph. Illford N30 plates have been used. The sample was placed in an absorption Cell which was a cylindrical quartz tube of diameter 2·5 cm. Three such tubes of different lengths were used. The two ends of the tube were sealed with quartz windows and this tube was placed in the path of the continuous radiation. Hydrogen arc lamp was used as the source of continuous radiation. Entire tube was wound with nichrome wire to vary the temperature of the vapour by passing a current through the wire.

3. Results

In the electronic spectra of 2,4-dichlorobromobenzene nearly sixty five bands have been measured. The bands are in general sharp and degraded towards red. Strong band at 2850·9Å (35066 cm^{-1}) has been identified as 0, 0 band of the system. The position of the bands with visual estimated intensity and their assignment has been given in table 1. Complete analysis has been done on the basis of three ground state (123, 203 and 427 cm^{-1}) and six excited state (219, 340, 494, 616, 930 and 1097 cm^{-1}) fundamental frequencies. Correlation of these electronic ground and excited state fundamental frequencies with those in infrared (Pandey & Singh 1975) is given in Table 2.

4. Discussions

Substitution of three halogen atoms in place of hydrogen atom in the ring at position 1, 2 and 4- reduces the symmetry of the molecule. Its only symmetry element is the molecular plane. Thus the molecule 2,4-dichlorobromobenzene has the lowest symmetry of the halogenated benzenes i.e., it belongs to the point group C_s which involves only two types of electronic and vibrational levels that are (i) symmetrical, and (ii) antisymmetrical to the molecular plane. All those symmetry classes of D_{6h} point group which are symmetrical to the molecular plane correspond to the symmetry class A' in the C_s point group. The A_{1g}–B_{2u} transition of benzene, in which both the states aere symmetric to the molecular plane corresponds to the transition A'–A'. This is symmetry allowed transition with its transition moment lying in the plane of the molecule.

From the simple group theoretical rule the most strong band at 2850·9Å (35066 cm^{-1}) longer wavelength side has been identified as 0, 0 band. It is shifted to the red by 42 cm^{-1} with respect to the 0, 0 band of the corresponding system of 1,2,4-trichlorobenzene (35108 cm^{-1}).

The excited state fundamental at 219 cm^{-1} in this molecule appears with weak intensity but combines with many other fundamentals to explain combination bands. This is assigned as the substituent senstive component of e_{2g} (608 cm^{-1}). The other component of this vibration has been identified at 0+340 cm^{-1} in the excited state only. Its counterpart in the ground state could not be observed.

The band corresponding to the excited state furdamental at 616 cm^{-1} is intense in the spectrum. This band is progression forming and combines with other fundamentals showing totally symmetric character. Therefore this has been correlated with the infrared frequencies at 805 cm^{-1} (1975) and assigned to ring breathing mode a_{1g} (992 cm^{-1}). Due to the interaction of a_{1g} (992 cm^{-1}) and b_{1u} (1010 cm^{-1}) modes of benzene (Ingold *et al* 1948 and Randle *et al* 1954)

Table 1. Analysis of the electronic absorption bands of 2,4-dichlorobromobenzene.

Band position cm^{-1}	Intensity+	Shift from 0, 0 band cm^{-1}	Assignment
34609	w	0−457	0−370−3×28
34639	w	0−427	0−370−2×28
34671	wd	0−395	0−370−28
34696	m	0−370	0−370
34715	wd	0−351	?
34749	wd	0−317	0−203−123
34780	wd	0−286	0−203−3×28
34802	wd	0−264	0−203−2×28
34830	m	0−236	0−203−28
34863	m	0−203	0−203
34888	w	0−178	0−123−2×28
34918	m	0−148	0−123−28
34943	ms	0−123	0−123
34975	wd	0−91	0−3×28
35008	ms	0−58	0−2×28
35038	ms	0−28	0−28
35066	s	0	0, 0
35109	mw	0+43	0+43
35136	mw	0+70	0+70
35167	mw	0+101	0+101
35199	wd	0+133	0+219−3×28
35228	wd	0+162	0+219−2×28
35256	wd	0+190	0+219−28
35285	w	0+219	0+219
35321	w	0+255	0+340−3×28
35340	w	0+274	0+340−2×28
35374	mw	0+308	0+340−28
35406	ms	0+340	0+340
35476	w	0+410	0+494−3×28
35512	wd	0+446	0+494−2×28

Table 1—Contd.

Band position cm^{-1}	Intensity†	Shift from 0, 0 band cm^{-1}	Assignment
35537	wd	0+471	0+494−28
35560	msd	0+494	0+494
35598	wd	0+532	0+616−3×28
35629	wb	0+563	0+616−2×28
35660	wb	0+594	0+616−28
35682	ms	0+616	0+616
35729	wb	0+663	0+616+43
35780	wb	0+714	0+2×370−28, 0+616+101
35811	w	0+745	0+2×370, 0+340+494−3×28
35852	w	0+786	0+340+494−2×28
35872	w	0+806	0+340+494−28
35902	w	0+837	0+340+494
35910	w	0+855	0+930−3×28
35935	mw	0+870	0+930−2×28
35965	w	0+899	0+930−28
35996	ms	0+930	0+930
36044	m	0+978	0+930+43
36106	ms	0+1040	0+1097−2×28
36138	msd	0+1072	0+1097−28
36163	sd	0+1997	0+1097
36187	w	0+1121	0+219+930−28
36215	w	0+1149	0+219+930
36246	vw	0+1180	0+930+340−3×28
36376	w	0+1210	0+930+340−2×28
36311	w	0+1245	0+930+340−28
36341	w	0+1275	0+930+340
36407	vw	0+1341	0+930+494−3×28
36437	w	0+1371	0+930+494−2×28
36472	w	0+1406	0+390+494−28
36494	w	0+1428	0+930+494
36576	w	0+1510	0+616+930−28
36616	w	0+1550	0+616+930
36771	w	0+1685	0+1097+616−28
36781	w	0+1715	0+1097+616
36096	w	0+2030	0+930+1097
37199	w	0+2133	0+2×1097−2×28
37230	w	0+2164	0+2×1097−28
37261	w	0+2195	0+2×1097

† v = very, s = strong, w = weak, m = medium, d = diffuse, b = broad.

Table 2. Correlation of the infrared and ultraviolet absorption frequencies of 2,4-dichlorobromobenzene.

Infrared frequencies	Ultraviolet frequencies G.S.	Ultraviolet frequencies E.S.	Assignment
	123		
	203		C-Cl out of plane bending
440		219	
	370		Component of e_{2g} (608 cm^{-1})
530		340	
670		494	C-Cl stretching
815		616	Ring breathing
1030		930	C-C-C trigonal bending
1160		1097	C-H planar bending

two combined breathing modes resulted. The value of the former, being substituent sensitive, is reduced much. The latter of the modified modes is easily identified at 930 cm^{-1} in excited state. The corresponding ground state value in electronic spectra has not been observed.

The strong and diffuse fundamental band on the shorter wavelength side of the 0, 0 band has been observed at 0+1097 cm^{-1}. This band appears upto double quanta with weak intensity and combined with a good number of fundamentals. In this range there are neither ring nor substituent vibration like C–Cl or C–Br. The vibration corresponding to this mode must be assigned to a C–H planar bending mode.

According to the previous works of Kohin (1949), Anno & Matubra (1956) and Srivastava (1968) on chlorinated benzenes the C–Cl stretching vibration should appear around 600 cm^{-1} and C–Br stretching vibration around 500 cm^{-1}. In the present study we have observed only one fundamental in this region at 0+494 cm^{-1}. On account of high electronegativity of Cl atom than bromine the intensity of C–Cl stretching should be stronger than C–Br. Therefore the band at 0+494 cm^{-1} has been assigned as C–Cl stretching vibration.

Most of the fundamentals and overtones are followed by satellites at separations of 28 cm^{-1} on the longer wavelength side of 0, 0 band. This has been taken to represent v–v transitions between the fundamentals of the two states.

0, 0 band shift :

From these studies (previous as well as present) it is concluded that the shift in pure electronic transition in chlorinated benzenes is in the order of monochlorobenzene < dichlorobenzene < trichlorobenzene < dichlorobromobenzene. The position of the 0, 0 band in some chlorosubstituted benzenes and their shift towards red with respect to benzene (Sponer 1939) has been given in Table 3. It has been observed that the shift in dichlorobromobenzenes is in order of 2,5-dichlorobromo < 3,4-dichlorobromo < 2,4-dichlorobromobenzene. It is remarkable that the shift of 0, 0 band in these dichlorobromobenzenes is nearly same with respect to benzene.

Table 3. Shift of 0, 0 band of some substituted benzene.

Molecule	0, 0 band cm^{-1}	Shift cm^{-1}	Reference
Benzene	38089		+
Chlorobenzene	37052	1037	
o-dichlorobenzene	36230	1859	
m-dichlorobenzene	36186	1903	
p-dichlorobenzene	35743	2346	
1,3,5-trichlorobenzene	35498	2591	
1,2,4-trichlorobenzene	35108	2981	
2,4-dichlorobromobenzene	35066	3023	Present
3,4-dichlorobromobenzene	35047	3042	++
2,5-dichlorobromobenzene	35043	3046	

+ H. Sponer and G. Nordhein 1939 *J. Chem. Phys.* **7**, 207.
* H. Sponer 1942 *Rev. Mod. Phys.* **14**, 224.
++ T. S. Varadarajan and A. K. Kakkor 1971 *Ind. J. Pure Appl. Phys.* **9**, No. 4.

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